



PATENT SPECIFICATION

NO DRAWINGS

1147.169

Inventors: RAYMOND CARPENTIER, NATHALIE STAS-SARIBAN
and CYRILLE VAN EYGEN

Date of filing Complete Specification: 29 Sept., 1967.

Application Date: 30 Sept., 1966.

No. 43758/66.

Complete Specification Published: 2 April, 1969.

© Crown Copyright 1969.

Index at acceptance:—C3 P(8C8B, 8C13A, 8C13B, 8C13C, 8C14A, 8C14B, 8D2A, 8D2B2, 8D4, 8D8, 8K8); C3 R(2C8P, 2C16, 2C25, 2C29, 2L1B, 2L2A, 2L2X, 2L6G, 2L6H, 29C6X, 29C8P, 29C16, 29C25, 29C29, 29L1A, 29L1B, 29L2A, 29L2X, 29L6G, 29L6H); D1 P(3E, 3F2, 3G4, 3G5)

Int. Cl.:—C 08 f 3/64

COMPLETE SPECIFICATION

Oil- and Water-Repellent Compositions

We, UCB (UNION CHIMIQUE-CHEMISCHE
BEDRIJVEN) SOCIÉTÉ ANONYME, of 4, Chaus-
sée de Charleroi, Saint-Gilles-lez-Bruxelles,
Belgium, a Body Corporate organised under
the laws of Belgium, do hereby declare the
invention, for which we pray that a patent
may be granted to us, and the method by
which it is to be performed, to be particularly
described in and by the following statement:—

The present invention is concerned with new
oil- and water-repellent compositions.

Our British Patent Specification No.
28800/65 (Serial No. 1,096,392), is concerned
with new fluorinated, ethylenically-unsaturated
mixed ester monomers and with their homo
and copolymers with one another or with co-
polymerisable olefinic compounds.

The homopolymers and copolymers thus
obtained have interesting oil-repellent prop-
erties which permit the consideration of their
use for the treatment of any porous or non-
porous material which is to be protected from
dirt and rendered resistant to wetting by water,
vegetable, animal or mineral oils or fats, hy-
drocarbons or organic solvents. However, the
water-repellent properties of these fluorinated
homopolymers and copolymers are not very
marked.

There exists, at present, a demand for finish-
ing agents which are capable of rendering
porous materials, in particular textile materi-
als, not only water-impermeable but also res-
istant to soiling by fatty materials. It is also
very important, for practical purposes, that
such compounds should have a permanent
character, i.e. that articles impregnated with
the said compounds should remain imperme-
able to water and fats, even after being sub-
jected to washing in an aqueous bath con-
taining soap and/or detergents or to dry-
cleaning with solvents.

By combining the polymerised fluorinated

olefinic compounds, which are the subject
matter of our above-mentioned Patent Speci-
fication, with suitable substances, we have
succeeded in preparing new compositions
which meet the above demands remarkably
well with regard to their oil-repellent and
water-repellent properties and to their perma-
nent character.

According to the present invention, there
are provided compositions for rendering porous
and non-porous materials oil-repellent and
water-repellent, which comprise a component
(A) in admixture into a component (B) and/or
with a component (C),

component (A) being selected from homo-
polymers of fluorinated, ethylenically-un-
saturated mixed esters of the general for-
mula:



wherein $R'CO_2$ is the residue of a perfluoro-
alkanoic acid,

$R''CO_2$ is the residue of a polymerisable
alkenoic acid, and

Y is a bivalent aliphatic, aromatic or ali-
phatic-aromatic radical the carbon chain
of which may be interrupted by oxygen
atoms,

and of copolymers selected from copolymers
of the said fluorinated ethylenically-un-
saturated mixed esters with one another and
of copolymers of the said fluorinated ethyl-
enically-unsaturated mixed esters with co-
polymerisable monomers selected from alkyl
acrylates, alkyl methacrylates, acrylamide
and methacrylamide,

component (B) being at least one copolymer
selected from the copolymers of alkyl acryl-
ates and alkyl methacrylates with an ethyl-
enically-unsaturated compound which con-
tains a reactive group selected from N-

methylol, N-alkoxymethyl, aldehyde and epoxy groups, and component (C) being at least one aminoplast resin selected from the polymeric products obtained by the reaction of NH_2 group-containing, compounds with aldehydes or with aldehydes and alcohols, particularly aminoplast resins obtained by the reaction of melamine or urea with formaldehyde, as well as their reaction products with alcohols, especially alkylated urea-formaldehyde and alkylated melamine-formaldehyde resins.

The compositions according to the present invention contain 1 to 50%, preferably 3 to 20%, by weight of the component (A), 0 to 99%, preferably 0 to 60%, by weight of the component (B) and 0 to 99%, preferably 0 to 60%, by weight of the component (C), at least one of components (B) and (C) being present.

The fluorinated ethylenically-unsaturated mixed esters and the homo- and copolymers of these compounds (which form component A of the compositions according to the present invention), as well as the preparation of these materials, form the subject matter of our British Patent Specification No. 28800/64 (Serial No. 1,096,392). Component (A) is preferably used in the form of a solution in organic solvents or of an aqueous emulsion or dispersion which generally contains 1 to 30% by weight of homo- and/or co-polymers.

Component (B) in the composition according to the present invention consists of at least one copolymer of alkyl acrylates and/or alkyl methacrylates with an ethylenically-unsaturated derivative having an N-methylol, N-alkoxymethyl, aldehyde or epoxy function.

Examples of acrylate and/or methacrylates which can be used for the preparation of these copolymers are hexyl, 2-ethyl-hexyl, *n*-heptyl, *n*-octyl and *n*-nonyl acrylates; and butyl, isobutyl, amyl, *n*-hexyl, *n*-heptyl, *n*-octyl, 2-ethyl-hexyl and *n*-nonyl methacrylates.

As examples of ethylenically-unsaturated derivatives with an N-methylol, N-alkoxymethyl, aldehyde or epoxy function, which can be copolymerised with the stated esters, there may be mentioned N-methylol-acrylamide and its alkylated derivatives, such as N-methoxymethyl-acrylamide, N-methylol-methacrylamide and its alkylated derivatives, such as N-methoxymethyl-methacrylamide, N-methylol-maleimide, acrolein, methacrolein and glycidyl acrylate and methacrylate. Component (B) contains 90 to 99.5% by weight of acrylates and/or methacrylates and 10 to 0.5% by weight of the ethylenically-unsaturated derivative having an N-methylol, N-alkoxymethyl, aldehyde or epoxy function.

Component (B) can be prepared by the methods commonly used for polymerisation in an organic solution or in an aqueous emulsion or dispersion in the presence of conventional polymerisation catalysts, such as inorganic or

organic peroxides, hydroperoxides, peracids, persalts, diazo compounds and redox systems. The polymerisation in an aqueous emulsion or dispersion is carried out in known manner in the presence of anionic, cationic and/or non-ionic surface-active agents, emulsion stabilisers and the like. Component (B) is preferably used in the form of an organic solution or of an aqueous emulsion or dispersion which contains 2 to 40% by weight of dry matter.

Component (C) in the compositions according to the present invention is an aminoplast resin selected from polymeric products which are obtained by reacting NH_2 group-containing compounds, such as melamine and urea, with aldehydes, such as formaldehyde, and possibly additionally with alcohols, such as methanol, ethanol and butanol. These resins, which are prepared by the usual methods, are preferably used in the form of aqueous solutions or emulsions or in the form of solutions in organic solvents, these solutions or emulsions containing 20 to 80%, by weight of dry matter.

As stated above, the compositions according to the present invention contain 1 to 50%, preferably 3 to 20%, by weight of component (A), 0 to 99%, preferably 0 to 60%, by weight of component (B), and 0 to 99%, preferably 0 to 60%, by weight of component (C).

In fact, these compositions usually also contain either solvents or water and, for example, surface-active agents and/or emulsion stabilisers. They are prepared by mixing the solutions, emulsions or dispersions of the components (A), (B) and (C) in the proportions defined above. The compositions thus obtained can be marketed as such or they can be concentrated by eliminating part of the solvent or water by evaporation, or they can be diluted by adding a certain quantity of solvent or water. In general, the total of essential components in the solutions, emulsions or dispersions according to the present invention amounts to 0.1 to 50% by weight, preferably 0.5 to 35% by weight. The compositions of the present invention can also be used in the form of aerosols.

In order to promote the cross-linking and the adhesion of the water-repellent and oil-repellent coatings to the materials which are to be rendered water- and oil-repellent, a catalyst is generally added to the compositions, for example, zinc nitrate hexahydrate or ammonium nitrate, in an amount of 1 to 30% by weight of the total of the components (A), (B) and (C).

With a view to their use for the impregnation of porous or non-porous materials which are to be rendered water- and oil-repellent, the solutions, emulsions or dispersions according to the present invention can be diluted either with an organic solvent or with water. The solutions, emulsions or dispersions thus diluted are called "baths". The concentration of these baths obviously varies in accordance with the

nature of the material to be impregnated and the weight of water- and oil-repellent resin which is to be fixed on the material. The total of essential components in the oil- and water-repellent baths according to the present invention amounts to 0.1 to 20%, preferably 0.5 to 10%, by weight of the baths.

The porous and non-porous materials which can be treated with the baths according to the present invention in order to be made oil- and water-repellent are, for example, natural or synthetic textile fibres and the fabrics produced therefrom, paper, wood, bricks, asbestos, materials of asbestos cement, concrete, leather and hides. The porous and non-porous materials are rendered impermeable to water and fats by impregnating them with the solutions, emulsions or dispersions according to the present invention. They are then dried at a temperature between 15 and 100°C. in order to evaporate the water or solvents and then subjected to a temperature of 130 to 180°C. for a period varying from 5 minutes to 15 seconds in order to fix the coating on the porous or non-porous materials in a durable manner.

Since the most important use of the compositions according to the present invention is to render fabrics oil- and water-repellent, the following statement is particularly concerned with the treatment of such material.

The fabric is padded in the bath described above and then squeezed between rollers. As a result of the pressure under which the fabric is squeezed between the rollers, the fabric absorbs a more or less large amount of the bath. If, for example, the weight of the fabric has increased by 70% after padding and

squeezing, its squeezing rate is stated to be 70%.

The fabric is subsequently air-dried for about 30 minutes or dried in a drying cabinet at 100°C. for a few minutes in order to evaporate the solvent or water.

The fabric is subsequently heated to a temperature of 130 to 180°C. for a period varying from 5 minutes to 15 seconds, the duration of the treatment being the shorter, the higher is the temperature.

The compositions according to the present invention offer important advantages in comparison with the known fluorinated compounds. Thus, an excellent oleophobia is achieved while using a substantially smaller amount of fluorinated polymer, the cost of the oil-repellent treatment being thus reduced. On the other hand, the coatings applied exhibit an excellent resistance to washing with soapy water or to dry-cleaning with solvents. Finally, the compositions according to the present invention permit the obtaining of an excellent hydrophobia. These properties will be proved in the following Examples.

The proof of the oleophobic properties of the compositions according to the present invention is carried out by using the scale of B. J. GRAJECK and W. H. PETERSON (Textile Research Journal, 32, (1962), 323). In this test, mixtures of paraffin and hydrocarbon (*n*-heptane) are first prepared in proportions by volume which are graded from 0% to 100% of paraffin and, correspondingly, from 100% to 0% of hydrocarbon, each mixture thus obtained being characterised by an oleophobia coefficient according to the following Table:

Oleophobia coefficient	Paraffin oil as %	Hydrocarbon (<i>n</i> -heptane) as %
50	100	0
60	90	10
70	80	20
80	70	30
90	60	40
100	50	50
110	40	60
120	30	70
130	20	80
140	10	90
150	0	100

The higher the coefficient, the less tendency has the fabric to be soiled by the mixture of oil and solvent. For the test, a drop of one of the above mixtures is placed on the substrate treated with the oleophobic composition and that drop is sought, which is richest in hydrocarbon and yet remains for at least 3 minutes on the substrate, i.e. without penetrating into the latter. The oleophobia test is considered to be satisfactory when the coefficient amounts to at least 90 and it is obviously better to the extent that the coefficient is higher.

In order to prove the hydrophobic properties of the compositions according to the present invention, the following methods are applied:

- a) Belgian standard 593.05 (BUNDESMANN) for the determination of the percentage of water absorption (this must be as low as possible, the maximum percentage tolerated being 25—30%) and the penetration of water into the fabric, expressed in cc. (this value depends on the texture of the fabric but, in principle, it should be nil or only slightly above zero);
- b) Belgian standard 593.06 for the determination of the degree of hydrophobia by the spray test; the results are expressed by arbitrary values, the value 80 being the lowest limit tolerated, whereas 90 is an acceptable value and 100 is an excellent value.

Finally, the tests for resistance to washing

and dry-cleaning are carried out according to the "Prescriptions de contrôle provisoire pour le symbole d'entretien lavage" (25th October 1962) and "Prescriptions de contrôle provisoire pour le symbole d'entretien dégraissage" (20th October 1962), respectively, which have been published by the Comité Technique International d'Etiquetage (C.T.I.E.)

The following Examples are given for the purpose of illustrating the present invention, the percentages being by weight unless otherwise stated:—

EXAMPLE 1.

In this Example, there is used a fabric consisting of 30% cotton and 70% polyester, which has a weight of 180 g./sq.m. and a density of 50 threads per cm. in the warp and 28 threads per cm. in the weft. Samples of this fabric are impregnated in baths containing various proportions of a homopolymer of 2,2-dimethyl-propane-1,3-diol perfluorooctanoate methacrylate (component A) and of a copolymer from 99% octyl methacrylate and 1% N-methylolacrylamide (component B). The samples are subsequently squeezed to a squeezing rate of 70%, then air-dried at room temperature for about 30 minutes and finally treated at 165°C. for 3 minutes.

The following Table indicates the percentage by weight of the compounds (A) and (B) applied to the fabric samples and the content of these components in the bath, stating each time the result obtained in the oleophobia test described above.

TABLE I

Component A (%)		Component B (%)		Oleophobia
applied to the fabric	in the bath	applied to the fabric	in the bath	
0.05	0.07	0.450	0.64	70
0.07	0.1	0.93	1.33	80
0.1	0.14	0.9	1.3	90
0.14	0.20	1.86	2.66	100
0.21	0.3	2.8	4	110
0.3	0.43	1.7	2.43	110
0.3	0.43	5.7	8.14	110
0.4	0.57	1.6	2.3	110
0.6	0.86	5.4	7.7	110
0.9	1.3	5.1	7.3	110

It can be seen from this Table that by applying only 0.1% by weight of the compound (A) to the fabric, there is obtained an oleophobia which corresponds to commercial standards. On the other hand, there is no advantage in applying more than 0.21% by weight of the compound (A) to the fabric, in order to achieve an oleophobia of 110. It can also be seen that the oleophobia is not affected by strong variations of the compound (B).

EXAMPLE 2.

In this Example, the fabric used and the working conditions are the same as in Example 1. However, there are used different polymeric fluorinated esters as compound (A) and different non-fluorinated copolymers as compound (B).

The following Table states the percentage by weight of compound (A) (compounds I to IX) present in the bath and that applied to the fabric, and the percentage by weight of the compound (B) (compounds X to XIII) present in the bath and that applied to the fabric, stating, in each case, the result obtained in the oleophobia test described above.

The polymers (A) are the following:

- I same polymer as in Example 1;
- II homopolymer of ethylene glycol perfluorooctanoate acrylate;

- III homopolymer of ethylene glycol perfluorooctanoate methacrylate; 30
- IV homopolymer of propylene-glycol perfluorooctanoate methacrylate;
- V homopolymer of 2-methyl-2-propylpropane-1,3-diol perfluorooctanoate methacrylate; 35
- VI homopolymer of 2,2-diethyl-propane-1,3-diol perfluorooctanoate methacrylate;
- VII homopolymer of diethylene glycol perfluorooctanoate methacrylate; 40
- VIII homopolymer of pentamethylene glycol perfluorooctanoate methacrylate;
- IX copolymer of 50% 2,2-dimethylpropane - 1,3 - diol perfluorooctanoate methacrylate and 50% 2,2-dimethylpropane-1,3-diol perfluorobutyrate methacrylate; 45

The polymers (B) are the following:

- X copolymer of 99% octyl methacrylate and 1% N-methylolacrylamide; 50
- XI copolymer of 99% 2-ethyl-hexyl acrylate and 1% N-methylol-acrylamide;
- XII copolymer of 99% butyl acrylate and 1% N-methylol-acrylamide; 55
- XIII copolymer of 96% 2-ethyl-hexylmethacrylate and 4% N-methoxymethylacrylamide.

TABLE II

Component A (%)				Component B (%)				Oleophobia
in the bath		applied to the fabric		in the bath		applied to the fabric		
I	(0.36)	I	(0.25)	XI	(3.2)	XI	(2.25)	110
I	(0.07)	I	(0.05)	XI	(1.36)	XI	(0.95)	90
I	(0.36)	I	(0.25)	XII +XI	(1.07) (0.7)	XII +XI	(0.75) (0.5)	110
I	(0.36)	I	(0.25)	XII	(1.8)	XII	(1.25)	110
I	(0.09)	I	(0.06)	XIII	(0.46)	XIII	(0.32)	90
II	(1.07)	II	(0.75)	X	(3.2)	X	(2.25)	90
III	(0.29)	III	(0.2)	XI	(2.6)	XI	(1.8)	110
III	(0.43)	III	(0.3)	XI	(1.3)	XI	(0.9)	100
IV	(1.07)	IV	(0.75)	X	(3.6)	X	(2.5)	110
V	(1.07)	V	(0.75)	X	(3.6)	X	(2.5)	110
V	(0.43)	V	(0.3)	X	(1.8)	X	(1.25)	110
V	(0.14)	V	(0.1)	X	(1.8)	X	(1.25)	90
VI	(1.07)	VI	(0.75)	X	(3.6)	X	(2.5)	110
VI	(0.14)	VI	(0.1)	X	(1.8)	X	(1.25)	110
VII	(0.43)	VII	(0.3)	X	(1.8)	X	(1.25)	110
VII	(0.14)	VII	(0.1)	X	(1.8)	X	(1.25)	100
VIII	(0.43)	VIII	(0.3)	X	(1.8)	X	(1.25)	100
IX	(0.86)	IX	(0.6)	X	(3.6)	X	(2.5)	110

5 This Table shows the extent to which the formulations of the compositions according to the present invention can be modified, while still obtaining an excellent oleophobia which corresponds to the commercial standards.

EXAMPLE 3.

10 The same mixed cotton/polyester fabric (30/70) is used and the working conditions are the same as in Example 1. However, there is used an aqueous impregnating solution which contains, per litre, 36 g. of an emulsion of the homopolymer of 2,2-dimethylpropane-1,3-diol perfluorooctanoate methacrylate containing 10% dry matter, 10 g. of an emulsion of the copolymer of ethylhexyl acrylate and

N-methylol-acrylamide (96/4) containing 20% dry matter and 90 g. of an emulsion of the copolymer of ethyl-hexyl methacrylate and N-methylol-acrylamide (96/4) containing 20% dry matter, as well as 5 g. of zinc nitrate hexahydrate as catalyst. After this treatment, the fabric contains 0.252 g. of fluorinated compound and 1.65 g. in all of resin per 100 g. of fabric.

25 In the following Table III, column 1 corresponds to the tests carried out on the new fabric, column 2 to the fabric washed according to the C.T.I.E. standard mentioned above and column 3 to the fabric dry-cleaned according to the C.T.I.E. standard also mentioned above.

TABLE III

Hydrophobia test	1	2	3
Bundesmann: water absorption as % penetration of water as cc.	22 0	18 0	20 0
Spray test:	100	90	100
Oleophobia test	100	100	100/110

5 The Table shows that this formulation according to the present invention satisfies the commercial standards of hydrophobia and oleophobia, even after washing and dry-cleaning.

EXAMPLE 4.

10 The fabric and the working conditions are the same as in Example 3. However, the 10 g. of the emulsion of the copolymer of ethyl-hexyl acrylate with N-methylol-acrylamide containing 20% dry matter and the 90 g. of the emulsion of the copolymer of ethyl-hexyl methacrylate with N-methylol-acrylamide containing 20% dry matter are replaced by 100

g. of an emulsion containing 20% dry matter of a copolymer obtained from 1.9 g. ethyl-hexyl acrylate, 17.3 g. ethyl-hexyl methacrylate and 0.8 g. N-methylol-acrylamide. As in Example 3, the solution also contains 5 g. of zinc nitrate hexahydrate as catalyst.

20 After this treatment, the fabric contains 0.252 g. of fluorinated compound and 1.65 g. in all of resin per 100 g. of fabric.

25 The following Table IV gives the results obtained on the new fabric (column 1), on the washed fabric (column 2) and on the dry-cleaned fabric (column 3).

TABLE IV

Hydrophobia test	1	2	3
Bundesmann: water absorption as % penetration of water as cc.	18 0	16 0	16 0
Spray test:	100	90	100
Oleophobia test	100	100/110	110

EXAMPLE 5.

30 The fabric and the working conditions are the same as in Example 3. However, there is added, in addition to the finishing composition of Example 3, 30 g. per litre of an aqueous solution containing 70% dry matter of a methylated melamine-formaldehyde resin which is marketed by us under the name "Synkamine MF" (component C). (Synkamine" is a Registered Trade-Mark). Here,

40 too, 5 g. of zinc nitrate hexahydrate are added per litre of bath. After the treatment, the fabric contains 0.252 g. of fluorinated compound and 3.12 g. in all of resin per 100 g. of fabric.

45 The tests for hydrophobia and oleophobia are carried out with new fabric (column 1), washed fabric (column 2) and dry-cleaned fabric (column 3). There are thus obtained the results set-out in the following Table V:

TABLE V

Hydrophobia test	1	2	3
Bundesmann: water absorption as % penetration of water as cc.	26 0	18 0	18 0
Spray test:	100	100	100
Oleophobia test	110	100	110

EXAMPLE 6.

This Example is the same as Example 3, except that the cotton/polyester fabric is replaced by a fabric of 85% Polynosic and 15% nylon. After the treatment, the fabric contains 0.252 g. of the fluorinated compound and

1.65 g. in all of resin per 100 g. of fabric. The tests refer again to new fabric (column 1), washed fabric (column 2) and dry-cleaned fabric (column 3). There are obtained the results set out in the following Table VI:

TABLE VI

Hydrophobia test	1	2	3
Bundesmann: water absorption as %	25	29	27
penetration of water as cc.	0	0	0
Spray test:	95	85	85
Oleophobia test	100	100	100

EXAMPLE 7.

This Example is the same as Example 3, except that the cotton-polyester fabric is replaced by a light nylon fabric and that the squeezing rate is 55% instead of 70%. After the treatment, the fabric contains 0.2 g. of the

fluorinated compound and 1.3 g. in all of resin per 100 g. of fabric. The tests again refer to new fabric (column 1), washed fabric (column 2) and dry-cleaned fabric (column 3). There are thus obtained the results set out in the following Table VII:

TABLE VII

Hydrophobia test	1	2	3
Bundesmann: water absorption as %	7	7	3.4
penetration of water as cc.	0	0	0
Spray test:	100	95	100
Oleophobia test	90/100	80/90	100

EXAMPLE 8.

This Example is the same as Example 3, except that the cotton/polyester fabric is replaced by a cotton fabric. After treatment, the fabric contains 0.252 g. of the fluorinated

compound and 1.65 g. in all of resin per 100 g. of fabric. The results are shown in the same manner as in Example 3 and are set out in the following Table VIII:

TABLE VIII

Hydrophobia test	1	2	3
Bundesmann: water absorption as %	33	35	36
penetration of water as cc.	0	0	0
Spray test:	95	85	85
Oleophobia test	100	100	100

EXAMPLE 9.

The fabric and the working conditions are the same as in Example 3. However, there is used an aqueous impregnating solution which contains, per litre, 11.6 g. of an aqueous emulsion containing 10% dry matter of a homopolymer of 2,2-dimethyl-propanol,3-diol

perfluorooctanoate methacrylate, 3.2 g. of an aqueous emulsion, containing 20% dry matter of a copolymer of ethyl-hexyl acrylate and N-methylol-acrylamide (96% and 4%, respectively), 29 g. of an aqueous emulsion containing 20% dry matter of a copolymer of

ethyl-hexyl methacrylate and N-methylol-acrylamide (96% and 4%, respectively), and 30 g. of an aqueous solution containing 70% dry matter of a methylated melamine-formaldehyde resin (obtained by the reaction of melamine, formaldehyde and methanol) which is marketed by us under the name of "Synkamine MF".

The bath also contains 5 g. of zinc nitrate hexahydrate as catalyst. After this treatment, the fabric contains 0.0813 g. of fluorinated compound and 2 g. in all of resin.

In the following Table, column 1 corresponds to the tests made with the new fabric, column 2 to those with washed fabric and column 3 to those with dry-cleaned fabric.

TABLE IX

Hydrophobia test	1	2	3
Bundesmann: water absorption as %	24	22	29
penetration of water as cc.	1	0	3
Spray test:	100	100	100
Oleophobia test	100	90	90

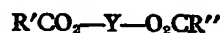
EXAMPLE 10.

In this Example, there is used a Kraft paper with a weight of 80 g./sq.m. A sample of this paper is impregnated in a bath containing, per litre, 30 g. of an aqueous emulsion containing 10% dry matter of a homopolymer of 2,2-dimethyl-propane-1,3-diol perfluorooctanoate methacrylate, 30 g. of an aqueous emulsion containing 20% dry matter of a copolymer of 2-ethyl-hexyl methacrylate and N-methylolacrylamide (96% and 4%, respectively), 15 g. of an aqueous emulsion containing 20% dry matter of a copolymer of 2-ethyl-hexyl acrylate and N-methylol-acrylamide (96% and 4%, respectively) and 34.4 g. of an aqueous solution containing 70% dry matter of the methylated melamine-formaldehyde resin "Synkamine MF". The bath also contains 8 g. of zinc nitrate hexahydrate as catalyst. The paper thus treated is then squeezed to a squeezing rate of 60%, air-dried for about 30 minutes and finally treated at 130°C. for 3 minutes. After this treatment, the paper contains 0.18 g. of the fluorinated compound and 2.17 g. in all of resin per 100 g. of paper. The oleophobia thus obtained corresponds to the value 110. Furthermore, when a strip of 3×10 cm. of treated paper is suspended vertically in such a manner that 3 mm. of the lower end are immersed in groundnut oil, it is found that the oil has not risen in the paper mass after 24 hours. When, on the other hand, the same test is applied to untreated Kraft paper, an immediate rising of the groundnut oil in the paper mass is observed and after 24 hours the paper is completely impregnated throughout.

WHAT WE CLAIM IS:—

1. Composition for rendering porous and non-porous materials oil-repellent and water-repellent, which comprises by weight, 1—50% of a component (A), 0—99% of a component (B) and 0—99% of a component (C), at least

one of components (B) and (C) being present, component (A) being selected from homopolymers of fluorinated, ethylenically-unsaturated mixed esters of the general formula:



wherein R'CO₂ is the residue of a perfluoroalkanoic acid,

R''CO₂ is the residue of a polymerisable alkenoic acid, and

Y is a bivalent aliphatic, aromatic or aliphatic-aromatic radical, the carbon chain of which may be interrupted by oxygen atoms,

and of copolymers selected from copolymers of the said fluorinated, ethylenically-unsaturated mixed esters with one another and of copolymers of the said fluorinated, ethylenically-unsaturated mixed esters with copolymerisable monomers selected from alkyl acrylates, alkyl methacrylates, acrylamide and methacrylamide,

component (B) being at least one copolymer selected from the copolymers of 90—99.5% by weight of alkyl acrylates and/or alkyl methacrylates with 10—0.5% by weight of an ethylenically-unsaturated compound which contains a reactive group selected from N-methylol, N-alkoxymethyl, aldehyde and epoxy groups, and component (C) being at least one aminoplast resin selected from the polymeric products obtained by the reaction of NH₂ group-containing compounds with aldehydes or with aldehydes and alcohols.

2. Compositions according to claim 1, wherein component (C) is an aminoplast resin obtained by the reaction of melamine or urea with formaldehyde or by the reaction of the product obtained with an alcohol.

3. Composition according to claim 1, where-

in component (C) is an aminoplast resin selected from alkylated urea-formaldehyde and alkylated melamine-formaldehyde resins.

4. Composition according to any of the preceding claims, comprising by weight 3 to 20% component (A), 0 to 60% of component (B) and 0 to 60% of component (C), at least one of components (B) and (C) being present.

5. Composition according to any of the preceding claims, wherein components (A), (B) and/or (C) are present in the form of a solution in organic solvents comprising 0.1 to 50% by weight of the components (A) + (B) and/or (C), 99.9 to 50% by weight of at least one organic solvent.

6. Composition according to claim 5, wherein components (A), (B) and/or (C) are present in the form of a solution in organic solvents comprising 0.5 to 35% by weight of the components (A) + (B) and/or (C) and 99.5 to 65% by weight of at least one organic solvent.

7. Composition according to any of Claims 1—4, wherein components (A), (B) and/or (C) are present in the form of an aqueous emulsion or dispersion comprising 0.1 to 50% by weight of the component (A) + (B) and/or (C) and 99.9 to 50% by weight of water.

8. Composition according to claim 7, wherein components (A), (B) and/or (C) are present in the form of an aqueous emulsion or dispersion comprising 0.5 to 35% by weight of the components (A) + (B) and/or (C) and 99.5 to 65% by weight of water.

9. Composition according to any of the preceding claims, which comprises 1 to 30% by weight of a cross-linking and adhesion catalyst, referred to the total weight of the components (A) + (B) and/or (C).

10. Compositions according to claim 1 for rendering porous and non-porous materials oil- and water-repellent, substantially as hereinbefore described and exemplified.

11. Bath for rendering porous and non-porous materials oil-repellent and water-repel-

lent, comprising 0.1—20% by weight of a composition according to claim 1 and 99.9—80% by weight of at least one organic solvent.

12. Bath according to claim 11, comprising 0.5—10% by weight of a composition according to claim 1 and 99.5—90% by weight of at least one organic solvent.

13. Bath for rendering porous and non-porous materials oil-repellent and water-repellent, comprising 0.1—20% by weight of a composition according to claim 1 and 99.9 to 80% by weight of water.

14. Bath according to claim 13, comprising 0.5—10% by weight of a composition according to claim 1 and 99.5 to 90% by weight of water.

15. Bath according to any of claims 11—14 for rendering porous and non-porous materials oil- and water-repellent, substantially as hereinbefore described and exemplified.

16. Process for rendering porous and non-porous materials oil-repellent and water-repellent, which comprises impregnating the material in a bath according to any of claims 11—14, drying the impregnated material at a temperature of between 15 and 100°C. to evaporate the solvent or water and to form a coating and subjecting the material to a temperature of 130 to 180°C. for a period varying from 5 minutes to 15 seconds.

17. Process according to claim 16 for rendering porous and non-porous materials oil- and water-repellent, substantially as hereinbefore described and exemplified.

18. Porous and non-porous materials, whenever rendered oil-repellent and water-repellent by means of a composition according to claim 1.

VENNER, SHIPLEY & CO.,
Chartered Patent Agents,
Rugby Chambers,
2, Rugby Street,
London, W.C.1,
Agents for the Applicants.